TERPENE STUDIES I

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Preface

The problem involved in this dissertation may be divided into four sections. Each division constitutes a chapter of the dissertation.

The first chapter describes the fractionating equipment developed for the purification of terpenes.

The second chapter is a presentation of the common physical properties of alpha and beta pinene and their mixtures.

The third chapter describes the action of selenium dioxide on beta pinene in various solvents and the method developed for the separation of carvopinone from pinocarvone, and the separation of these ketones from alcohols and esters produced by the reaction. A proposal as to the structure and means of formation of some of the products of this reaction is given.

The fourth chapter describes the preparation of an azo dye from rosin. This dye is a derivative of dehydroabietic acid.

Chapter I

PERFORMANCE OF SOME DISTILLATION COLUMNS FOR THE FRACTIONATION OF TERPENES

Introduction

Raw gum gathered from pine trees is separated at the turpentine still into turpentine and rosin. The turpentine is a complex mixture, consisting largely of terpene hydrocarbons[1,2] of the bicyclic mono terpene series. The rosin obtained consists largely of abietic acid with some resinous materials generally called resene.[3]

In general, the most practical way to separate and purify hydrocarbons of like nature is by fractional distillation. It is by this process that a- and B- pinene are obtained commercially from gum and wood turpentine.

The commercial production of a- and B- pinene does not yield pure substances, but fractions that are rich in one or the other of these compounds. These fractions in some cases contain impurities boiling less than three degrees apart. For research purposes it is essential to have as pure a starting material as possible. Thus a research laboratory working with terpene hydrocarbons needs fractionating equipment capable of producing a desired terpene in a high state of purity.

Before any experimental work could be carried out with a- or

B-pinene, these substances had to be obtained as pure as possible. In all cases this was done by the fractionation of commercial material.

Since a- and B- pinenes do not have widely separated boiling points, it was necessary that efficient columns be used for their separation and purification. This instigated a study of different types of fractionating columns and column packing.

Many fairly efficient columns have been reported.[4] Among these are columns packed with Raschig rings, Berl saddles, single turn glass helices, the concentric glass tube column of Selker, Burke and Lankelma,[5] the spiral screen packing of Lecky and Ewell,[6] Stedman cones, and the Podbelniak type. The cost of the latter two made their extensive use undesirable. The concentric glass tube type, although having a very low operating holdup and height equivalent to a theoretical plate, did not have a high capacity and also required better conditions of heat insulation than were feasible to construct in this laboratory. Experimentation showed that the single turn glass helices would not operate satisfactorily for terpenes under the conditions of column control used. Of all the types of packing encountered, only the Raschig rings, Berl saddles and the spiral screen seemed suitable. Columns of these packings were constructed and subjected to performance tests.

General Column Construction and Operation

A glass tube was filled with the desired packing and surrounded by a concentric glass tube which was wrapped with nichrome wire in such a manner as to produce about 125 watts for the entire length of column. The packed column and heater jacket were then inserted in a large glass tube which served as an insulator. After standard taper glass joints were welded onto the column, it was then mounted and was ready for use.

All kettles used in connection with the columns were electrically heated. The electrical heat energy supplied, for kettle and column, was controlled by transformers.

The columns were all regulated so that the column temperature was within two degrees of the temperature of the vapors in the head. The rate of throughput, or return through the head or reflux, was regulated by the rate of evaporation of liquid from the kettle.

In all performances listed the column was operating at a head return that gave it its maximum efficiency.

Performance Tests

The number of plates of all columns was determined by the use of n-heptane methylcyclohexane and the data of Beatty and Calingaert[7] and Bromily and Quiggle.[8] This was measured as H.E.T.P. which is the column height equivalent to one theoretical plate.[9]

The determination was made by refluxing the binary test mixture

in the column until equilibrium existed between liquid and vapor successively throughout the column. When equilibrium was reached, a few drops of the condensed vapor were withdrawn from the head; simultaneously a few drops were drawn from the kettle. These were analyzed for content by the use of a refractometer. From the refractive indices, the total number of plates in the column were determined by consulting the data in Table I.

For example, a refractive index at the head of 1.3920 corresponds to 76 plates, and a refractive index in the kettle of 1.4055 to 55 plates, then the total number of plates in the column is 76-55 or 21 plates.

The data given in Table I is obtained by combining the two equations

$$n_D^{20} = 1.4232 - 0.0410x + 0.00555x^2$$

an experimental equation to express mole fraction of heptane, x, in mixtures of heptane and methyl cyclohexane in terms of refractive index, and

$$n = \frac{\log \frac{x_o(1-x_n)}{x_n(1-x_o)}}{\log R}$$

in which n = number of theoretical plates

x_o = mole fraction heptane in liquid

x_n = mole fraction heptane in liquid, but less than x_o

R = volatility ratio; the quotient of the vapor pressures of the more volatile to less volatile component, which

in this case is heptane and methyl cyclohexane, at the temperature midway between their boiling points. Its value here is 1.07.

and is derived from theoretical considerations in the following manner.

Let: P_a = pressure of more volatile component at a given T.

P_b = pressure of less volatile component at same T.

y = mole fraction of A, more volatile, in vapor phase.

x = mole fraction of A, more volatile, in liquid phase.

Then by Raoult's law:

$P_a = P_a x$ and p_a is proportional to y

$P_b = P_b(1-x)$ p_b is proportional to (1-y)

hence;

$$\frac{y}{1-y} = \frac{P_a}{P_b}\frac{x}{1-x}$$

so

$$\frac{y}{1-y} = R\frac{x}{1-x}$$

and solving for x:

$$y(1-x) = Rx(1-y)$$

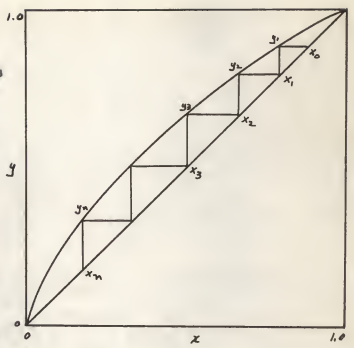
$$Rx = y + Rxy - xy$$

$$x(R - Ry + y) = y$$

$$x = \frac{y}{R - Ry + y} = \frac{1}{R(1/y - 1) + 1}$$

Now considering the step diagram given on the next page, it is plain that vapors y_1 have the same composition as liquid x_0 and that liquid x_1 will give rise to vapors y_1, hence going from liquid x_0 to x_1 involves one theoretical plate. Thus x_0, x_1, x_2, x_n are values of

x corresponding to n = 0, 1, 2, ---n. and taking x_n as less than x_0, then:



To go from x_1 to x_0 n = 1;

$$x_1 = \frac{1}{R(1/y_1-1) + 1}$$

and since vapors y_1 when condensed give liquid x_0, $y_1 = x_0$; likewise $y_2 = x_1$; so

$y_2 = 1/R(1/x_0-1) + 1$

and to go from x_2 to x_0, n = 2

$$x_2 = \frac{1}{R(1/y_2-1) + 1} \quad \text{or} \quad \frac{1}{R(R(1/x_0-1)_{,1} - 1) + 1}$$

$$x_2 = \frac{1}{R^2(1/x_0-1) + 1}$$

In like manner it can be shown that for any number of theoretical plates, R is raised to that power. Hence, in general, from x_n to x_0:

$$x_n = \frac{1}{R^n(1/x_0-1) + 1}$$

When n = 0; a condensation process is represented by a horizontal line and,

$$x_0 = y_1 = \frac{1}{(1/x_0-1) + 1}$$

Solving the general equation for n:

$$R^n = \frac{x_0(1 - x_n)}{x_n(1 - x_0)} = w$$

$$n \log R = \log w$$

$$n = \frac{\log \frac{x_0(1 - x_n)}{x_n(1 - x_0)}}{\log R}$$

then by arbitrarily starting with $x_n = 0.02$, and changing x_0 by 0.04 at a time the data of Table I was calculated.

Non-drainable holdup is measured by pouring a known volume of benzene through the packing and collecting the liquid drainings in a graduated cylinder. The difference between these volumes is the non-drainable holdup. This is recorded in Table III for the test columns.

Operating holdup of the column is the volume of liquid present in the column during any instant of a distillation. To measure this quantity a weighed amount of a non-volatile compound such as stearic acid was dissolved in a weighed amount of a volatile compound such as benzene, and the mixture refluxed in the column under operating conditions. A sample of several grams was then withdrawn from the distilling flask and weighed. The benzene was then removed from the sample on a steam bath and the sample was weighed again. These two weighings were used to calculate the change in the per cent of stearic acid in the flask from which the weight of benzene remaining in the flask was determined. This weight subtracted from the weight of benzene originally present in the flask was the weight of the benzene present in the column while in operation. Conversion of weight to volume gives operating holdup as listed in Table III. This

is an important factor in analytical distillations where column holdup must be small with respect to the volume of mixture being analyzed.

Pressure drop is the difference in pressure in the head and in the kettle. A column with a high resistance to vapor flow has a large pressure drop, an undesirable feature if thermal reaction should set in. Pressure drops are measured by connecting a manometer alternately to the head and kettle by means of a double diagonal stopcock.

Construction and Performance of Raschig Ring and Berl Saddle Packed Columns

A four-foot length of glass tubing with an inside diameter of 0.43 inch was filled with 4 x 4 mm. Raschig rings and tested for efficacy. This is column 1. The tube was then emptied of Raschig rings and filled with 4 x 4 mm. Berl saddles and again tested for efficacy. This is column 2.

Column 3 was made by filling a 2½ ft. glass tube with inside diameter of 0.75 inch with 4 x 4 mm. Berl saddles.

The results of the efficiency tests on this and columns 1 and 2 are tabulated in Tables II and III.

No data is available in the literature for 4 x 4 mm. Berl saddles but mention has been made of the unsatisfactory results obtained when 4 x 4 mm. Raschig rings are used for analytical columns.[10] Both these packings give essentially the same H.E.T.P. and the same

holdup per plate for a four-foot column of 0.43 inch inside diameter. Due to their high operating holdup these columns could not be used for analysis. When a column of 0.75 inch inside diameter was filled with these Berl saddles, the H.E.T.P. decreased to 1.3 inches. This value is comparable with the best values reported for other loose packings[4] with the exception of single turn stainless wire helices[11] which have an H.E.T.P. of less than one inch. These data and the fact that these columns operate satisfactorily with the distillation of terpenes at 20 mm. pressure, indicate that either packing is satisfactory for purification of components in the more readily separable terpene mixtures. Furthermore, these data also indicate that Berl saddles are a very efficient packing to obtain fractions rich in a desired component from a given raw material in as short a time as possible. Since these packings are loose they may be transferred from one column to another, thus the same packing may be utilized for different purposes. In some cases Berl saddles should not be used because of the catalytic nature of their unglazed porcelain surface.

The Construction and Performance of the Spiral Screen Packing

Laboratory Columns for Large Quantities of Material

The first column was made using 60 x 60 mesh stainless steel wire gauze and a glass tube with an inside diameter of 1.50 inches and having an inner tube of 0.40 inch outside diameter all according

to the specifications of Lecky and Ewell.[6]

Washers of stainless steel wire gauze were made with an outside diameter of 1.50 inches and an inside diameter of 0.40 inch. One-eighth inch of the outer edge of the washer was cupped at an angle of 40 degrees. A sector of approximately 20 degrees was removed from each washer and the washers were spot-welded together into a spiral group of twenty-four. By joining these groups in a similar manner, any desired length could be obtained. This spiral was then placed on the inner tube which was made from glass of outside diameter of 0.40 inch. A stiff wire spiral spacer, made of one-eighth inch iron wire, with five turns to the inch, was screwed into the gauze spiral. Long stiff rods were welded to the ends of the spacer to permit pulling as well as pushing of the spiral into the large glass tubing. At intervals during the insertion, the exposed gauze spiral was tightened on the inner tube in order to insure a more uniform fit. When the insertion of the spiral was completed, the spacer was removed by unscrewing it. Standard taper glass joints were then welded to the column and the column placed in a heating and insulating jacket. When this column was tested for plate efficiency it was found to have an H.E.T.P. of 4.6 inches. Since it was noted that the washers did not fit tightly against the outer wall, it was decided that a tighter fit could be obtained by increasing the diameter of the inner tube, and thus decrease the flexibility of the gauze washer.

Washers were then made with outside diameter of 1.50 inches and inside diameter of 0.71 inch. From these washers a column was assembled in the manner above. This operation lowered the H.E.T.P. to 2.8 inches.

This was still a very unsatisfactory column. After close inspection, it was noted that the washers still did not fit snugly against the outer wall. It was thought then that grinding the edges of the gauze spiral would give a more uniform fit. Thus the spiral screen packing of the previously described column was removed, placed on a mandrel, ground in the direction of the spiral to a diameter just 1/32 inch larger than the glass tube into which it was to be inserted. Upon assembly this column showed an H.E.T.P. of 1.3 inches. This showed a marked improvement over the original column and emphasized the importance of a uniform and tight fit to the outer wall of the column. While an H.E.T.P. of 1.3 inches is satisfactory for many purposes, it does not satisfy the requirements of terpene work.

In order to produce a still tighter fit against the outer wall, washers were made from 50 x 50 mesh stainless steel wire gauze having an outside diameter of 1.50 inches and an inside diameter of 0.71 inch. The washers were assembled and ground in the manner described. This produced such a tight fit that two outer jackets burst while an attempt was made to insert the spiral screen packing. When the packing was inserted and the column set up for use it was

found that the H.E.T.P. was 0.66 inch. This is column 4 of Tables II and III.

Due to the large size of this column it was not practical to make the operating holdup measurement. In order to determine this, a column 23 inches long with identical construction was tested. The data was: Original concentration of stearic acid 10.2%; original weight of mixture 67.9 g.; final concentration of stearic acid 16.8%. This corresponds to an operating holdup of 33.5 cc. of benzene. Thus column four should have an operating holdup of 67 cc. of benzene, since it possesses twice as many turns as the shorter column tested.

Laboratory Columns for Small Quantities of Material

For the separation of small quantities of material, high efficiency and a small diameter are necessary.

For this purpose stainless steel washers having an outside diameter of 0.40 inch and an inside diameter of 0.10 inch were made from 60 x 60 mesh stainless steel wire gauze. These washers had a cup of 1/16 inch around the outer edge. Nickel wire was used as the inner rod and the spacer used had seven turns to the inch. This was assembled in the manner previously described, except for the grinding of the spiral which was not necessary for a column of this small diameter. This is column 5 of Table II and shows an H.E.T.P. of 0.72 inch. In assembling this column it was necessary to replace all faulty washers in the spiral with new ones, as flooding frequently occurred in the vicinity of the faulty washer. As is true

with all columns of small diameter, the operation must be carefully controlled or flooding will occur.

In order to prepare a column with a small holdup and yet with a rather high capacity stainless steel washers were made with outside diameter of 0.71 inch and inside diameter of .25 inch from 50 x 50 mesh gauze. The spirals were assembled and ground and inserted into the outer glass tube in the manner described above. The spacer used had seven turns to the inch. A two-foot length of this type construction will show an H.E.T.P. of 0.40 inch under optimum conditions and an H.E.T.P. of 0.60 inch under easily controlled conditions. Only under extremely poor operating conditions will this column display an H.E.T.P. of greater than 0.60 inch. This column does not readily flood and has a reasonably high capacity, being able to analyze at the rate of about 50 ml. per 24 hours. This is column 6 of Table II.

Operation of Columns

The columns were thoroughly wetted down with the liquid mixture and the column temperature was adjusted to within two degrees of the boiling point of the more volatile component. The columns were then kept on total reflux until liquid-vapor equilibrium was attained. This equilibrium may be judged by the constancy of the temperature of the condensing vapors. The kettle heat is so regulated that the reflux through the head is approximately half of that rate where

flooding occurs. This runs between one and five drops per second depending on the size of the column. A reflux ratio comparable to the efficiency of the column[12] and the mixture being separated was used. Reflux ratio is defined as the amount of condensed vapor returned to the column divided by the amount of condensed vapor collected in a given period of time. This is done by counting drops returned and collected for a certain time interval. If the volume of the drops is known the reflux ratio may be calculated.

When operating column 4, Table I, at a head reflux of 2.5 ml./min. and a reflux ratio of 25 to 1, only 200 ml. of liquid were required to pass from pure a-pinene to pure B-pinene at 20 mm. pressure. A batch of about 4000 ml. of commercial a-pinene was used in the kettle in this separation. This distillation is shown in Figure I.

Camphene which boils about equidistant between a- and B-pinene at 20 mm. pressure can be readily separated by the use of a six-foot length of the same size packing as column 4. In this separation a head reflux ratio of 40 to 1 used during the collection of a-pinene (boiling point 51.8° at 20 mm.) was purposely maintained throughout the transition from a-pinene to camphene (boiling point 55.5° at 20 mm.) This transition required 110 ml. In the transition from camphene to B-pinene (boiling point 59.2° at 20 mm.) the head reflux ratio was changed to 60 to 1 and had a transition volume of 85 ml., which is 15 ml. less than the operating holdup of

the column. 100 ml. of the camphene obtained had a solidifying range of 44-45° and the remainder solidified at a temperature not lower than 25° C. The distillation of about 800 ml. of mixture was completed in nine days. This distillation, shown in Figure II, indicates how this column might be used for rapid analysis of large quantities.

For distillations such as this a modified total condensation - partial takeoff head[13] was used. The condenser was a four-foot length of 0.5 inch outside diameter glass tubing bent into a spiral four inches high. A condenser such as this was necessary because of long periods of use, low temperature of vapors and the relatively high temperature of the tap water which was used for cooling the condenser. In some cases it was necessary to circulate brine through the condenser in order to minimize vapor loss.

As a preliminary test of column 5 a mixture of 35 ml. of carbon tetrachloride and 35 ml. of cyclohexane was separated into approximately 90 mole per cent carbon tetrachloride and 100 mole per cent cyclohexane. The holdup was 13 ml. and the operation required thirty-six hours. This distillation is shown in Figure III.

When fractionating terpenes the column was so regulated that the head reflux was about 0.8 ml./min. A head reflux ratio of 25 to 1 was used for collecting pure materials, and 40 to 1 for passing between fractions. The low pressure drop of this column combined with its high capacity minimizes any thermal reaction by allowing an

analysis to be completed in a short period of time.

32 ml. were collected from a mixture of a-pinene and B-pinene distilled through column 5 at 20 mm. pressure. Under the above described operating conditions 16 ml. of a-pinene, 11 ml. of B-pinene and 5 ml. of mixture boiling between the two pure components were obtained, as shown by Figure IV.

Column 5 has been used in the analysis of a mixture of terpene alcohols having a relative viscosity of 31. The operation of this column at 20 mm. for a material of this viscosity is almost as easy as the operation for a mixture whose relative viscosity is much less, such as a- and B-pinenes. This ease of operation with such viscuous materials makes the spiral screen type of column particularly valuable in the analysis of many terpene mixtures.

Costs of Spiral Screen Type

The entire cost of column 4, including all jackets and standard taper glass joints was $37.00; of column 5, $35.00. Labor costs including overhead were calculated at the rate of $1.50 per hour. Two work-hours per foot on column 4 and four work-hours per foot on columns 5 were required. These costs do not include the construction of the punches for cutting the washers which requires about 15 hours each.

TABLE I

DATA FOR DETERMINING THEORETICAL PLATES USING
n-HEPTANE METHYL CYCLOHEXANE

x_o	x_n	n	n^{20}_D
.02	.02	0.00	1.4224
.06	.02	16.86	1.4207
.10	.02	25.06	1.4191
.14	.02	30.71	1.4176
.18	.02	35.06	1.4160
.22	.02	38.83	1.4145
.26	.02	42.08	1.4130
.30	.02	45.06	1.4115
.34	.02	47.74	1.4100
.38	.02	50.31	1.4085
.42	.02	52.77	1.4070
.46	.02	55.16	1.4055
.50	.02	57.54	1.4041
.54	.02	59.91	1.4027
.58	.02	62.31	1.4013
.62	.02	64.78	1.3999
.66	.02	67.34	1.3985
.70	.02	70.06	1.3972
.74	.02	73.00	1.3959
.78	.02	76.25	1.3946
.82	.02	79.96	1.3933
.86	.02	84.37	1.3920
.90	.02	90.02	1.3908
.94	.02	98.21	1.3896
.98	.02	115.07	1.3883

TABLE II

PLATE DETERMINATIONS

Column No.	Column Packing	Column Specifications	Refractive Index of Head	Refractive Index in Kettle	Total No. of plates	H.E.T.P.
1	4 x 4 mm. Raschig rings	I. D. 11 mm. Packing height 46 in.	1.4005	1.4130	22	2.1
2	4 x 4 mm. Berl saddles	I. D. 11 mm. Packing height 48 in.	1.3970	1.4110	24	2.0
3	4 x 4 mm. Berl saddles	I. D. 19 mm. Packing height 27 in.	1.4045	1.4154	21	1.3
4	50 x 50 mesh Stainless steel spiral screen	I. D. 37 mm. Inner glass tube O.D.11 mm. Packing height 46 in.	1.3888	1.4164	70	0.66
5	60 x 60 mesh stainless steel spiral screen	I. D. 10 mm. Inner nickel rod, O.D. 2.5 mm. Packing height 46 in.	1.3910	1.4196	64	0.72
6	50 x 50 mesh stainless steel spiral screen	I. D. 17 mm. Inner glass tube, O.D. 6 mm. Packing height 15.5 in.	1.3930 1.3906 1.3909	1.4121 1.4123 1.4058	37 46 34	0.42 0.34 0.45

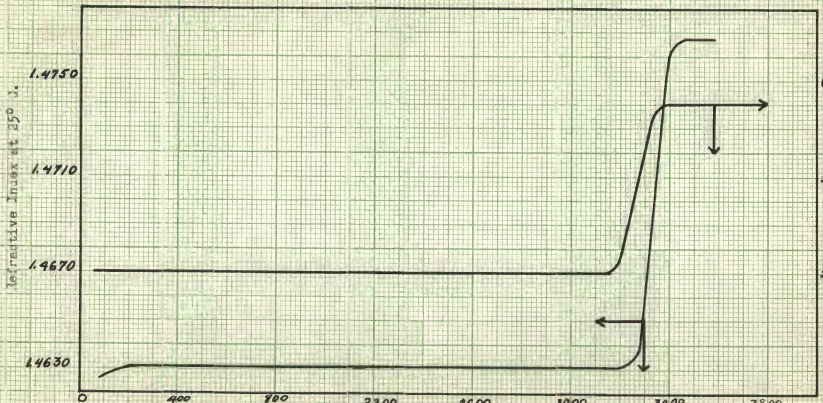
TABLE III

HOLDUP AND PRESSURE DROP DETERMINATIONS

Column No.	Non-Drainable Holdup ml.	Operating Holdup				Pressure Drop mm.
		Weight Test Mixture, g.	Initial % Stearic Acid	Final % Stearic Acid	Operating Holdup, ml.	
1	10	24.7	10.2	17.5	11.4	
2	8	19.7	9.75	21.0	12.1	
3	11	35.0	10.7	17.6	15.3	
4	28[1]					2
5	5[2]	23.8	10.5	15.9	9.1	2

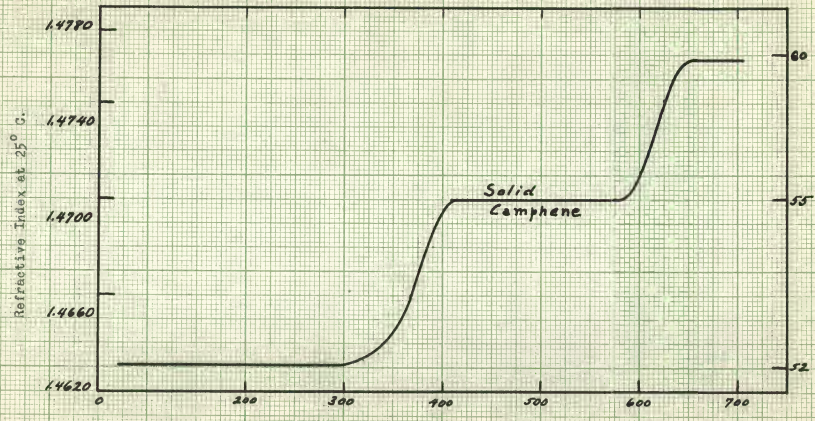
1. Non-drainable holdup, B-pinene, 40 ml.
2. Non-drainable holdup, B-pinene, 7.5 ml.

FIGURE I



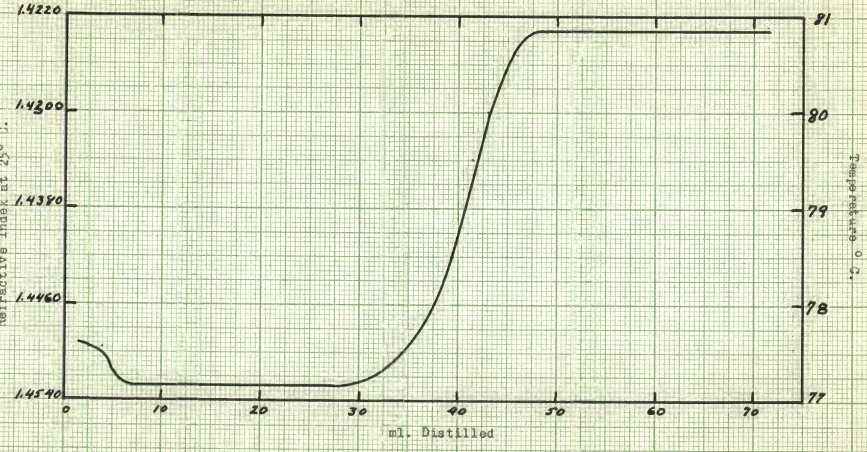
Separation of α- and β-pinene at 20 mm. with column 4

FIGURE II



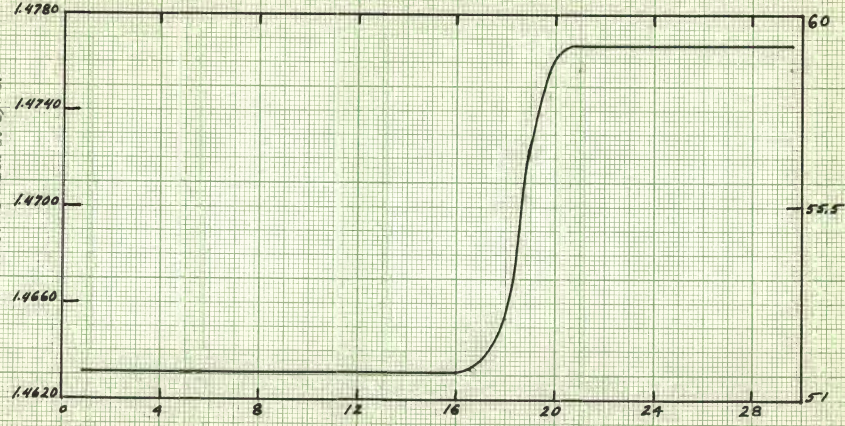
Separation of a-pinene, camphene and B-pinene at 22 mm. pressure with column 4

FIGURE III



Separation of carbon tetrachloride from cyclohexane at atmospheric pressure with column 5

FIGURE IV



Separation of α-pinene from β-pinene at 20 mm. pressure using column 5

Summary

A review of some column packings has been made with respect to their usefulness for the separation of terpenes. From this study and from experimentation it has been shown that the spiral screen packing is very efficient for the separation of terpenes, and that Berl saddles are the most efficient of any of the loose packings. A detailed account of the construction and operation of columns for the separation of terpenes has been given.

Chapter II

PHYSICAL CONSTANTS OF a- AND B-PINENE

A knowledge of the physical properties of binary mixtures of a- and B-pinene is very useful when working with American gum turpentine. Palkin[1] has pointed out that it is largely a- and B-pinene and is camphene free. This means thay any fraction between a- and B-pinene is a mixture of these two substances.

It may be observed by reference to sources of tabulated data such as Beilstein or the International Critical Tables that the values for the physical constants of a- and B-pinenes show a wide discrepancy. In order to make a study of binary mixtures of a- and B-pinene it was necessary first to establish constants for the pure substances.

In the first chapter it was shown that the spiral screen type of column packing was well suited for the purification of the pinenes. Thus by using efficient columns such as these it is possible to prepare a- and B-pinenes that are quite pure. Pinenes prepared by use of these columns should be of a higher degree of purity than any previously reported material. This is due to the rapid growth in the technology of column construction in the past few years.

Preparation of Pure a-Pinene and B-Pinene

a-Pinene was prepared by fractionation of commercial a-pinene

from gum turpentine through a 75 plate spiral screen column at 20 mm. pressure. This pressure was used to take advantage of the lower temperatures required to boil the pinenes so that thermal changes would be reduced to a minimum. Fractions were collected at 75 ml. intervals. All fractions with a refractive index at 25.0° C. in the range 1.4631-1.4633 were combined and refractionated through the same column. Fractions were then collected at 50 ml. intervals and their indices and optical rotations were measured at 25.0° C. The fractions which had identical physical values were combined and were considered to be pure a-pinene. In verification of this, a 100 ml. portion of the pure material was distilled through a 60 plate column. No change in the two physical constants was noted at any point during the collection of the distillate.

Wood turpentine is obtained by an extraction process from pine stumps. a-Pinene from wood turpentine is dextro rotatory and with a rather constant value of about + 26°. This in contrast with a-pinene from gum turpentine which may be either dextro or laevo rotatory of varying magnitude.[14] Thus it was quite desirable to obtain pure a-pinene from wood turpentine and to see if there was any difference in the physical properties. Simonsen[14] has pointed out that there could be a cis and trans form of a-pinene, although definite evidence of these have not been obtained. It was thus possible that an a-pinene from a different source, obtained in a

different manner, could have a different geometrical configuration.

The B-pinene used was prepared in an analogous manner from commercial B-pinene from American gum turpentine.

The fractionation of pure a-pinene from wood turpentine involves its separation from a small amount of camphene.[2] Camphene boils about 3° C. higher than a-pinene at 20 mm., thus a column of about 125 plates is best for this separation. The pinene fractions having constant refractive index and optical rotation at 25.0° C. were combined and refractionated. The distillate having constant physical properties was of the same purity as the a-pinene from gum turpentine.

These purified pinenes had the following constants:

Pinene	b. p. 20 mm.	$n^{25.0}_{D}$	$d^{25.0}_{4}$	$a^{25.0}_{D}$
a-gum	51.6	1.4631	0.8542	-3.83
a-wood	51.6	1.4631	0.8542	+26.10
B-gum	59.3	1.4768	0.8666	-21.49

These constants are in close agreement with unpublished data of Bain[15] and with much of the data of Palkin and Coworkers[1,2] of the United States Department of Agriculture. Most all of the data of the earlier workers[16] show variation from the above constants and in such a manner as to indicate that their a-pinene was contaminated with B-pinene, and that their B-pinene contained a-pinene. This is quite likely the case as efficient fractionating columns have only recently been developed.

Density Measurements

All density measurements were made with a 25 ml. density bottle and checked to the fourth decimal place by using two samples. The thermostat was held at 25.0° C. by means of an Aminco Metostatic Thermoregulator connected to the vacuum tube relay circuit developed by Hirshberg and Huntress.[17] The thermoregulator maintained the temperature within a limit of 0.02° C.

Mixtures of α- and β-pinene were made up to known concentration by weight. Measurements of the change in density with concentration were made using both gum and wood α-pinene. No difference in density was observed for these two α-pinenes at a given concentration of β-pinene. These data are given in Table IV and may be expressed at 25.0° C. by the equation:

$$d^{25}_4 = 0.8542 + 0.0129x - 0.0005\,x^2 \qquad (1)$$

in which x is the mole fraction of β-pinene.

Refractive Index Measurements

The refractive indices were obtained for the pure substances and then mixtures by using an Abbe refractometer which was calibrated against a known glass. Constant temperature was maintained by circulating water through the refractometer. The temperature of this water was controlled by the thermo regulator and vacuum tube circuit mentioned above.

Refractive index measurements on the two pure substances for

the temperature range 15-35° C. show that both a-pinene and B-pinene have a coefficient of 0.00045 units per degree. Observations were made every two degrees. The relation between temperature and refractive index is linear as shown by Table V.

The variation of refractive index with concentration for mixtures of B-pinene with either gum or wood a-pinene at 25.0° C. are given in Table VI. These data may be expressed by the equation:

$$n^{25.0}_D = 1.4631 + 0.0144x - 0.0007\,x^2 \qquad (2)$$

where x is the mole fraction of B-pinene.

The molar refractions of the pure components were calculated using the standard atomic refraction values of Auwers and Eisenlohr[18] and a value of 0.48[19] for the cyclobutane ring. In this manner a value of M_D of 43.99 is calculated for both a- and B-pinene. From observed data the M_D values of 43.93 and 44.40 were calculated for a- and B-pinene, respectively, by use of the Lorentz-Lorenz equation,

$$M_D = \frac{M}{d} \cdot \frac{n^2-1}{n^2+2}$$

where M_D = molar refraction

M = molecular weight

d = density at a given temperature

n = refractive index at same temperature for D-line.

The exhaltation of 0.41 for B-pinene is probably due to the presence of the exocyclic double bond since Auwers[20] has proposed that values of from 0.32 to 0.52 M_D unit be added to correct for the exocyclic

methylene group.

Polarimetric Measurements

Since a-pinene from gum turpentine has a rotation that varies with its source, sample, and the time of year obtained from the tree[21] the value of this constant has no diagnostic significance. It has been pointed out by Darmois[22] that B-pinene has a constant specific rotation regardless of its source, and that this value is -22.44° for Hg_j light.

All rotations were observed at 25.0° C. in a jacketed two decimeter tube. The polarimeter was equipped with suitable filters depending on the wave length of the light used.

Listed in Table VII are the specific rotations of a- and B-pinene and their mixtures for the Na_D (589 mm.), Hg_j (578 mm.), and Hg_v (546 mm.) lines. Also given are the observed rotatory dispersion which is the quotient of the rotation for one wave length divided by the rotation for another wave length.

Also listed in Table VII are the deviation of Biot's law for the linearity of specific rotations of mixtures from the observed value for the Na_D line. The deviations for the Hg_j and Hg_v lines are about the same. The data for change in rotation with concentration could be expressed by a second degree equation, however, this relation would change with the variation in the value of the rotation of the a-pinene used.

Biot's law may be applied, to express rotatory dispersion for a given mixture, in the form

$$\frac{a_V}{a_D} = \frac{n_B(a_B)_V + (1-n_B)(a_a)_V}{n_B(a_B)_D + (1-n_B)(a_a)_D}$$

in which n_B is the mole fraction of B-pinene in the mixture

$(a_B)_V$ is the specific rotation of B-pinene for Hg_V line

$(a_B)_D$ is the specific rotation of B-pinene for Na_D line

$(a_a)_V$ is the specific rotation of a-pinene for Hg_V line

$(a_a)_D$ is the specific rotation of a-pinene for Na_D line.

When the values of dispersion are calculated on this basis only a slight variation from the observed dispersions are noted. This deviation is illustrated for the $\frac{a_V}{a_D}$ dispersion by the data in column 7 of Table VII.

It is noteworthy to mention the observation of Dupont[22] that for mixtures of high a-pinene content, 70 mole percent or greater, the dispersion is a good indicator of the a-pinene content. Ordinarily the a_V/a_J ratio has been used, probably because the two lines are obtained from the same source. However, the data shows that a_V/a_D gives a wider dispersion range and therefore should give a more satisfactory indication of a-pinene content.

Vapor Pressure Measurements

Vapor pressures were determined only for pure a- and pure B-pinene. These were determined by the use of a distilling column in

which the vapors were allowed to come to equilibrium with the liquid. The column temperature was adjusted to within 1.5° of the temperatures of the condensing vapors in the head of the column. The temperatures of the condensing vapors were measured by the use of a calibrated mercury thermometer that could be read within a limit of ± 0.05° C. The bulb of the thermometer was wrapped with a single layer of cotton gauze.

The pressures were controlled accurately by a sulfuric acid manostat of the Hershberg-Huntress type.[17] The action of the vacuum pump on the manostat was checked by partially closing a stopcock placed between the pump and the manostat. Fluctuation was minimized by placing a five gallon bottle between the manostat and the system.

A mercury manometer was connected to the column head so that the pressure at which the vapors were condensing would be recorded. This manometer could be read to 0.1 mm. of mercury and was calibrated against a Germann[23] type of barometer.

At each recorded temperature 5 ml. of liquid was collected at a reflux ratio of 20 to 1.

The data thus obtained for α- and β-pinene in the pressure range of 15-80 mm. are recorded in Tables VIII and IX. These data were plotted on single cycle semilog paper, figures V and VI, and a straight line was drawn through the points. From this it was found that the equation

$$\log p = 8.0520 - 2193/T \qquad (3)$$

represents the data for α-pinene. Similarly, the equation

$$\log p = 8.0870 - 2256/T \qquad (4)$$

represents the data for β-pinene.

The Clausius-Clapeyron equation may be written as[44]

$$\frac{d \ln p}{d T} = \frac{L_e}{RT^2}$$

where L_e is latent heat, of vaporization in this case

R is the gas constant, 1.98 cal.

T is absolute temperature

p is pressure.

Assuming L_e to be constant, then integration gives

$$\ln p = -\frac{L_e}{RT} + c$$

thus $\log p = c - a/T$

where c and a are constants.

Hence $L_e = 2.3 \times R \times a$.

Thus from the slopes of the plots the latent heat of vaporization for the stated pressure range may be shown to be 10,040 cal. per mole or 73.72 cal. per gram for α-pinene and 10,320 cal. per mole or 75.84 cal. per gram for β-pinene.

Vapor-Liquid Compositions

The isobaric vapor-liquid compositions at 20.0 mm. were measured using a modified Smoshima apparatus.[24] This apparatus is designed to give one theoretical plate, so that the condensed vapors

would have the composition required by Raoult's law if the mixture were ideal. About 100 ml. of a mixture of a- and B-pinene were placed in the flask of the apparatus which was in a thermostat whose temperature was 2-4° above the estimated boiling point at 20mm. of the mixture in the flask. The pressure was then lowered to 20.0 mm., and the mixture was kept vaporizing constantly by means of an internal electrical heater. Equilibrium between liquid and vapor was generally obtained in two hours, but four hours were allowed before a final measurement was made. During this time a constant rate of flow of about 1.5 ml. per minute was maintained by the condensed vapors returning to the flask.

Due to the long periods of time allowed for equilibrium, brine was circulated through the condensing system which consisted of a pair of coils from four foot lengths of glass tubing. This condensing system was effective inasmuch as experiments showed that there was no detectible vapor loss four hours after vapor-liquid equilibrium was attained.

When equilibrium had been thoroughly established, samples of liquid and condensed vapor were withdrawn by means of a capillary pipette. The composition of the samples was determined by the use of the refractive index data Table X and equation 2. Measurements were made by starting with mixtures rich in B-pinene and going to mixtures rich in a-pinene, and also by starting with mixtures rich in a-pinene and going to mixtures rich in B-pinene. The data obtained

are given in Table X.

In order to compare the observed values with those of an ideal system, pressures of the pure components were calculated for the temperatures listed in Table XI using equations 3 and 4. Then for each temperature was calculated a liquid composition and its corresponding vapor composition at 20 mm. pressure by applying Raoult's law. The difference between the observed and calculated vapor composition is then a measure of the mixture's deviation from ideality. This deviation is given in Table XI.

When the data given in Table X are plotted in the form of a liquid vapor diagram, Figure VII, it is found that 24 theoretical plates are required to go from a mixture of 5 mole percent to 95 mole percent alpha pinene in a single fractional distillation. An estimated 43 theoretical plates are needed in order to make a complete separation within the limits of physical observation.

Column Tests

Since the vapor-liquid data for a- and B-pinene was available for 20 mm. pressure it was desirable to estimate the effect of throughput upon the efficacy of the column and also to test, at reduced pressure, the equation of Garswell,25 for H.E.T.P. of a packed column.

$$H.E.T.P. = kMd/T$$

where k is a constant for the column
M is the molecular weight of the liquid mixture
d is the density of the liquid mixture at the boiling temperature
T is the absolute boiling temperature of the liquid mixture.

The column chosen for this was a spiral screen type with an H.E.T.P. of 0.65 inch for the mixture, n-heptane-methylcyclohexane. Using this value, k was calculated to be 3.72. Accordingly an H.E.T.P. of 1.3 inch was expected for the mixture, a-pinene-B-pinene. Actually, see Table XII, a value of 0.75 inch was found as the maximum H.E.T.P., but if the throughput was increased or decreased appreciably from its optimum of 1.5 ml. per min. the H.E.T.P. rose to about 1.0 inch. Thus it appears from these data that the equation of Garswell's does not apply very well at reduced pressures and that the throughput has a critical range where the H.E.T.P. is least.

TABLE IV

DENSITIES OF MIXTURES OF a- AND B-PINENE

Mole Fraction B-pinene	$d^{25.0}_4$ obs.	$d^{25.0}_4$ calc.
0.000	0.8542	0.8542
.162	.8562	0.8563
.292	.8579	0.8579
.402	.8593	0.8593
.497	.8605	0.8605
.623	.8621	0.8621
.703	.8630	0.8630
.846	.8647	0.8648
1.000	.8666	0.8666

TABLE V

CHANGE OF REFRACTIVE INDEX WITH TEMPERATURE

t° C.	n_D α-pinene	n_D β-pinene
13.7	1.4682	1.4818
17.9	1.4663	1.4800
20.1	1.4653	1.4789
24.0	1.4636	1.4772
27.3	1.4621	1.4758
30.4	1.4607	1.4743
34.5	1.4588	1.4725
25.1	1.4631	1.4768

TABLE VI

REFRACTIVE INDICES OF α- AND β-PINENE

Mole Fraction β-pinene	$n^{25.0}_D$ obs.	$n^{25.0}_D$ calc.
0.000	1.4631	1.4631
.095	1.4645	1.4645
.203	1.4660	1.4660
.300	1.4673	1.4674
.400	1.4687	1.4687
.493	1.4700	1.4700
.588	1.4713	1.4713
.694	1.4727	1.4727
.781	1.4739	1.4739
.902	1.4755	1.4755
1.000	1.4768	1.4768

TABLE VII

SPECIFIC ROTATIONS AND DISPERSIONS OF MIXTURES OF α- AND β-PINENE

Mole Fraction β-pinene	$(\alpha)_D^{25.0}$	Dev.	$(\alpha)_j^{25.0}$	Dev.	$(\alpha)_v^{25.0}$	Dev.	$(\alpha)_v/(\alpha)_D$	Dev. $\times 10^3$	$(\alpha)_v/(\alpha)_j$
0.000	-3.83	---	-4.03	---	-4.57	---	1.193	---	1.134
.110	-5.69	-0.08	-5.96	-0.04	-6.59	-0.04	1.158	+9	1.106
.205	-7.32	- .13	-7.61	-0.10	-8.29	- .12	1.132	+4	1.091
.290	-8.71	- .24	-9.02	- .22	-9.77	- .23	1.121	+4	1.084
.394	-10.53	- .26	-10.85	- .25	-11.67	- .27	1.107	0	1.076
.495	-12.26	- .31	-12.61	- .30	-13.53	- .30	1.103	+2	1.074
.581	-13.84	- .25	-14.19	- .27	-15.17	- .27	1.097	+1	1.070
.680	-15.67	- .17	-16.05	- .19	-17.13	- .16	1.093	+1	1.067
.806	-17.90	- .16	-18.32	- .18	-19.50	- .15	1.089	+1	1.064
.887	-19.44	- .06	-19.86	- .09	-21.09	- .08	1.085	0	1.062
1.000	-21.49	---	-21.98	---	-23.28	---	1.083	---	1.059

TABLE VIII

VAPOR PRESSURE OF α-PINENE

t°C.	Pobs. mm.	Pcalc. mm.
84.0	82.1	82.0
80.8	71.8	71.9
77.7	63.3	63.4
73.2	52.7	52.6
68.3	42.7	42.7
60.9	30.8	30.7
59.3	28.6	28.6
54.1	22.5	22.5
52.3	20.6	20.6
46.9	15.8	15.9

TABLE IX

VAPOR PRESSURE OF B-PINENE

t°C.	Pobs. mm.	Pcalc. mm.
91.8	80.2	80.5
88.4	70.8	70.5
84.5	60.4	60.3
80.0	50.0	50.1
74.7	40.0	40.0
71.5	35.0	34.9
68.3	30.3	30.2
67.0	28.5	28.5
64.1	25.0	25.0
62.6	23.4	23.4
61.3	22.0	22.0
59.3	20.0	20.0
54.4	15.8	15.9

TABLE X

LIQUID-VAPOR COMPOSITION AT 20 mm.

α-pinene in Liquid		α-pinene in Vapor	
$n^{25.0}_D$	Mole fraction	$n^{25.0}_D$	Mole fraction
1.4759	0.070	1.4757	0.085
1.4758	0.075	1.4756	0.090
1.4754	0.105	1.4751	0.130
1.4751	.130	1.4747	.160
1.4747	.160	1.4742	.195
1.4745	.175	1.4740	.215
1.4731	.280	1.4722	.345
1.4727	.310	1.4718	.375
1.4722	.345	1.4712	.420
1.4718	.375	1.4708	.450
1.4713	.415	1.4702	.495
1.4710	.435	1.4699	.515
1.4706	.465	1.4694	.555
1.4698	.525	1.4686	.610
1.4691	.575	1.4680	.655
1.4689	.590	1.4678	.670
1.4680	.655	1.4671	.720
1.4676	.680	1.4667	.745
1.4668	.740	1.4661	.790
1.4662	.780	1.4656	.825
1.4653	.845	1.4649	.875
1.4650	.865	1.4647	.890
1.4648	.880	1.4645	.905
1.4647	.890	1.4644	.910
1.4641	.930	1.4639	.945
1.4637	.955	1.4636	.965

TABLE XI

DEVIATION OF VAPOR CONCENTRATION AS CALCULATED BY RAOULT'S LAW

$t^{o}C.$	Mole fraction a-pinene in liquid calc.	Mole fraction a-pinene in vapor calc.	Mole fraction a-pinene in vapor obs.	Vapor Dev. $x10^{2}$
52.0	0.945	0.962	0.964	-0.2
53.0	.796	.848	.836	1.2
54.0	.652	.728	.720	0.8
55.0	.516	.605	.602	0.3
55.4	.463	.553	.548	0.5
56.0	.385	.474	.464	1.0
57.0	.260	.334	.318	1.6
58.0	.142	.191	.174	1.7
59.0	.028	.040	.036	0.4

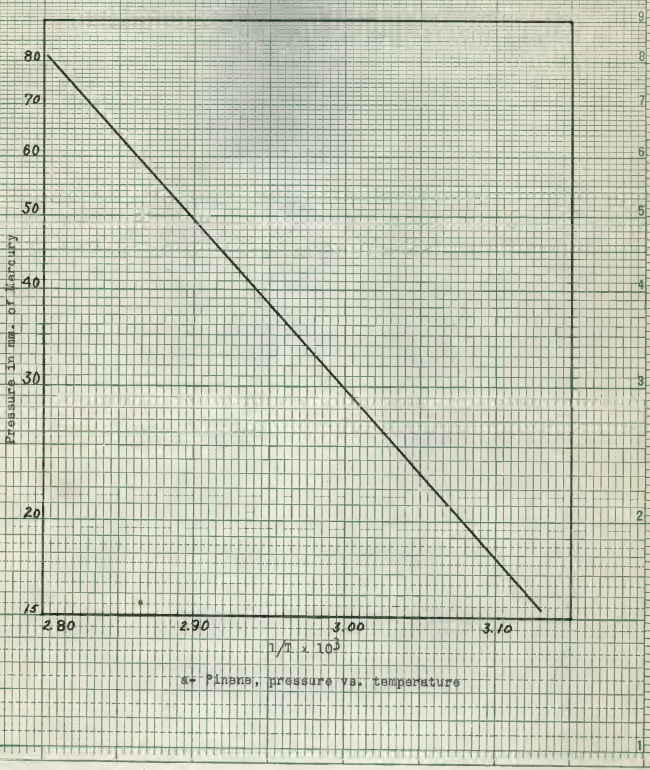
TABLE XII

H.E.T.P. VS. THROUGHPUT USING A MIXTURE OF a- AND B-PINENE

AT 20.0 mm. PRESSURE

Kettle Index	Head Index	Plates n ± 1	Throughput ml./min.
1.4749	1.4639	17	0.8
1.4749	1.4640	17	1.0
1.4761	1.4647	19	3.3
1.4758	1.4639	20	4.3
1.4759	1.4640	21	2.15
1.4763	1.4636	25	1.50
1.4756	1.4636	22	1.36

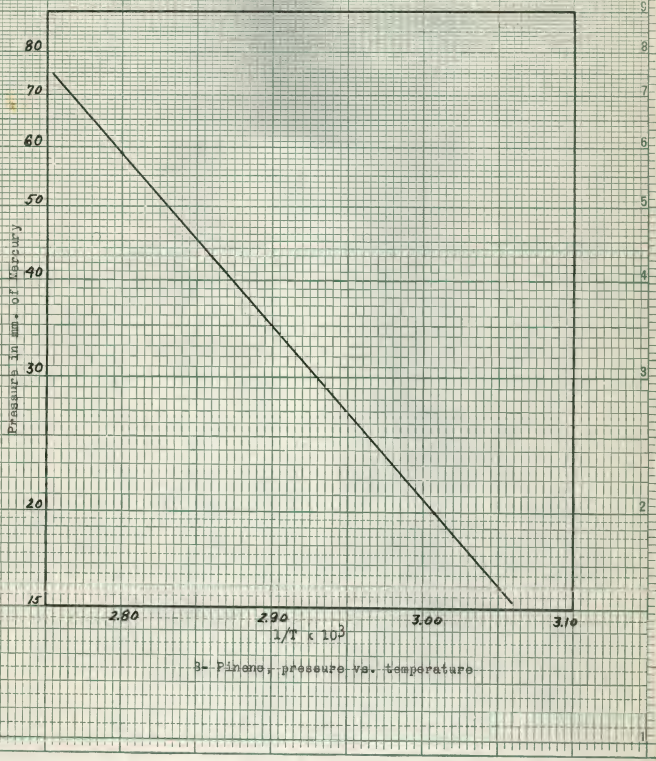
FIGURE V



α- Pinene, pressure vs. temperature

Semi-Logarithmic Paper.

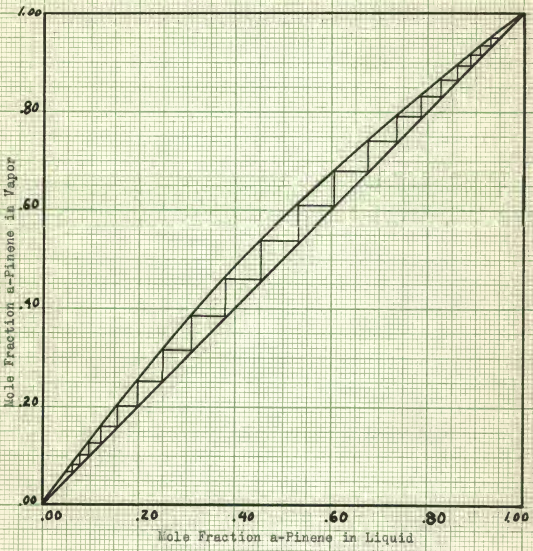
FIGURE VI



3- Pinene, pressure vs. temperature

Semi-Logarithmic Paper.

FIGURE VII



Vapor-liquid equilibrium diagram for α- and β- pinene at 20.0 mm.

Summary

In this chapter densities, refractive indices, and rotations of a- and B-pinene and their mixtures have been recorded.

The vapor pressure-temperature relation for a-pinene and B-pinene for the pressure range 15-80 mm. has been given.

The isobaric vapor-liquid equilibrium concentration data for mixtures of a- and B-pinene have been recorded. By means of these data it was shown that the system of a- and B-pinene is only ideal in the range 40-60 mole percent and has a rather wide departure from ideality at low or high mole percents.

A comparison between the H.E.T.P. as measured with n-heptane-methylcyclohexane and a- and B-pinene has been given.

Chapter III

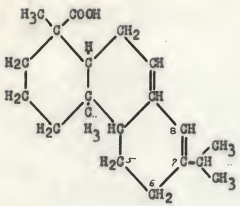
THE ACTION OF SELENIUM DIOXIDE ON B-PINENE

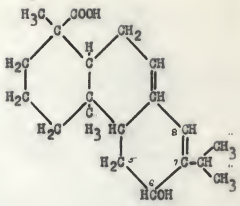
Introduction

Selenium dioxide has a selective action on ethylenic hydrocarbons. The double bond present in the ethylenic hydrocarbon activates the hydrogens on an adjacent methylene or methyl group. Selenium dioxide is unique in that it does not attack the point of unsaturation but does attack the methylene or methyl group that is activated by the ethylenic linkage[26]. In a compound where a methyl and a methylene group may be activated, it has been found that in general the methylene group is the group which is the more completely attacked. The primary product of the reaction is an alcohol; a secondary alcohol resulting from a methylene group and a primary alcohol from a methyl group. In many cases the reagent effects the oxidation of ketones and aldehydes to the corresponding α-diketone or α-keto aldehyde. In this manner glyoxal may be prepared from ethanal[27].

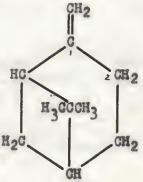
$$CH_3CHO \xrightarrow{SeO_2} OHC\text{-}CHO$$

In some cases the reaction stops with the formation of the hydroxy compound, an example of this is the preparation of 6-hydroxyabietic acid[28]. In this example the 6- position is activated by a conjugate system of double bonds rather than a single ethylenic link.

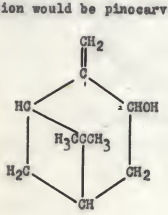




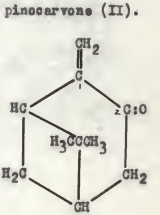
B-pinene has the structure:



Only the hydrogens on carbon at two are activated for reaction with selenium dioxide. Hence the products expected from the reaction would be pinocarveol (I) and pinocarvone (II).



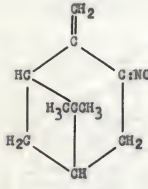
(I)



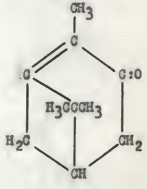
(II)

The action of selenium dioxide on B-pinene was originally carried out by Dupont, Allard and Dulou[19], who identified the steam volatile oil as pinocarvone. Since it appeared that pinocarveol should be among the products, this reaction was critically reexamined.

When B-pinene was treated with selenium dioxide in molar amounts in any solvent listed except acetic acid or acetic anhydride the resulting steam volatile oil was found to always be ketonic in nature. It proved to be a mixture of pinocarvone and carvopinone (IV).



(III)



(IV)

Carvopinone is a rather remarkable compound in that its existence is contrary to the Bredt rule[29] which states that substances having an ethylenic linkage attached to a dicyclic ring are unstable and tend to isomerize to a more stable form.

Until the present work, the only known preparation of carvopinone involved the formation of nitrosopinene (III) and its hydrolysis to carvopinone[30]. This hydrolysis only takes place to a very limited extent, hence large amounts of carvopinone have not been obtained.

Preparation of Selenium Dioxide

Selenium of 99% purity was dissolved in an excess of concentrated nitric acid in the hood. This solution was then evaporated to dryness over a steam bath. When dry it was dissolved in water, filtered and again evaporated to dryness. This was again dissolved in water, filtered and evaporated. When dry it was heated at 125° C for 2-4 hours and then pulverized in a mortar. When prepared in this manner the product was quite free from nitric acid and ready for use.

Preparation of B-Pinene

In all cases this was obtained by the fractionation of commercial material. As estimated by refractive index measurements the purity was between 99 and 100%. Since it has been found that B-pinene is rather rapidly attacked by air on standing[31], freshly distilled material was always used. Constants for a representative sample of B-pinene used were, b. p. 59° C (20 mm.), n^{25}_{D} 1.4768 $(\alpha)^{30}$ D -21.4°.

Oxidation of B-Pinene by Selenium Dioxide

Oxidations in Non-Esterifying Media.

The B-pinene and the solvent in the amounts shown in Table XIII were placed in a two-neck flask equipped with a stirrer and a reflux condenser. The powdered selenium dioxide was then slowly

added. Care must be taken to avoid too rapid an addition as this will cause the reaction to take place with explosive violence. It was found most practicable to add the selenium dioxide at a rate such that the reaction flask was never uncomfortably warm to the touch. After complete addition of the dioxide, the mixture was kept boiling gently, by means of an electrical heating jacket, for various lengths of time as indicated in Table XIII. When pyridine was used as a solvent a reaction temperature of 80-90° C was used. In general, heating for longer than ten hours decreased the yield of steam volatile oil and increased the yield of polymerization products. When the reaction was complete, the selenium formed was removed by filtration. The filtrate was steam distilled until a clear distillate was obtained. The ether extract of the distillate was then distilled at 2-3 mm. pressure in order to remove all solvent. The amounts and specific rotations of the oils thus obtained are shown in Table XIII.

In only one reaction was any hydrocarbon recovered. Here the recovery was less than 2% of the steam volatile oil.

In a few cases the residue after removal of the steam volatile oil was pyrolyzed and distilled under reduced pressure. The oil thus obtained had the odor characteristic of the alkyl sulfides and was not further investigated.

Oxidations in Esterifying Media.

B-pinene and the solvent in the amounts shown in Table XIV were rapidly stirred while selenium dioxide was slowly added. The rate of addition was such that the temperature of the mixture did not rise above 70° C. After addition of the SeO_2 the mixture was gently refluxed for four hours. At the end of this time the mixture was filtered to remove selenium and the filtrate steam distilled. The distillate was then treated with sodium bicarbonate and the oil extracted with ether and then distilled at 2-3 mm. pressure. This is the yield of oil recorded in Table XIV.

Method for Separation of Pinocarvone and Carvopinone

The oil containing a mixture of pinocarvone and carvopinone was added to twice its volume of a solution which contained 325 g. of sodium bisulfite and 105 g. of sodium bicarbonate per 1000 g. of water. Three to five drops of phenolphthalein indicator solution were added and the mixture shaken until the solution turned pink. Portions of 35% sodium bisulfite solution were added and the shaking repeated after each addition. This process was continued until the solution no longer became pink. At this point there was no oil visible. The solution was twice extracted with ether and the aqueous portion was then diluted

with twice its volume of water. The mixture was steam distilled with intermittent additions of saturated sodium carbonate solution until no more oil was obtained in the distillate. The volatile oil obtained by extraction of the distillate with ether was then distilled at 2-3 mm. pressure. The product was pinocarvone. It was identified by its oxime and its semicarbazone.

To the remainder of the hot sodium bisulfite solution was added 10 cc. of 25% sodium hydroxide and the steam distillation was continued. Ten cc. portions of sodium hydroxide were added intermittently until no more oil appeared in the distillate. During this process from 10 to 25% of the original oil was converted into a solid polymer in the bisulfite solution. The ether extract of the distillate was distilled at 2-3 mm. pressure. The product was carvopinone. It was identified by its semicarbazone, which yields carvone on hydrolysis and by its oxime which is nitrosopinene.

This is the manner in which the oils of Table XIII were separated.

Alcohol Tests for Oxidations of Table XIII

The oils in Table XIII were tested for alcohols because it was thought that some should be present. Since all of the tests described below were negative, it must be concluded that if alcohols are formed in the reaction between molar amounts of

B-pinene and selenium dioxide, they are present in undetectible amounts.

The tests described below were applied to the original oil obtained by the oxidation and to the ether extracts of the bisulfite solution and to the steam distillate obtained by adding sodium hydroxide to the bisulfite solution on the chance that neutral bisulfite might have added to the ethylenic linkage as in the case of propenol.[32]

One to two cc. portions of the various oils were shaken with 25% sulfuric acid and allowed to stand, with intermittent agitation, for several weeks. No crystalline hydrate was formed.

One cc. portions of the oils were treated with equal quantities of phenyl and α-naphthyl isocyanates, with and without solvents. No urethans formed.

One cc. portions of the oils were treated with acetic anhydride and sodium acetate. No acetates formed.

Separation of the Steam Volatile Oil from Oxidation Mixtures in Esterifying Media

These oxidations were carried out in acetic acid media in order to esterify any alcohol that might be formed - and in this manner obtain a more accurate insight as to the course of the reaction. For reactions carried out in acetic acid, the steam volatile products were found to be pinocarvone, carvopinone, and pinocarveol, largely as the acetate. The amounts of

each for a given reaction are shown in Table XIV. The following procedure was used to obtain these products.

For pinocarveol. The steam volatile oil from the oxidation mixture was added to an equal volume of ethyl borate[33] and heated for one hour at 125° C. and then by gradually lowering the pressure and raising the temperature to 150° C. the non-alcoholic materials were removed. Separate experiments have shown that butyl borate may be used equally well as ethyl borate. Previous experiments with pinocarvyl acetate showed that no pinocarvyl borate can be formed from the acetate under the above described conditions. After removal of the non-alcoholic materials, the residue in the flask is impure pinocarvyl borate. The borate was then simultaneously hydrolyzed and steam distilled from a 10% sodium carbonate solution. The volatile oil obtained in the distillate was extracted with ether and distilled at 2-3 mm. pressure to give quite pure pinocarveol.

For pinocarvyl acetate. The oil removed by distillation from the ethyl borate treatment was then added to twice its volume of sodium bisulfite solution and extracted as described for the separation of carvopinone and pinocarvone. When the ketonic materials were absorbed by the bisulfite solution, the solution was twice extracted with ether and the ether extract was distilled at 2-3 mm. pressure. The distillate was nearly pure pinocarvyl acetate.

For carvopinone and pinocarvone. These ketones were present in the bisulfite solution and were obtained from it by the selective decomposition of the bisulfite addition compounds already described.

No hydrocarbon was found in any of the reactions carried out in acetic acid media.

The reaction mixture may also be readily separated by first extracting with bisulfite and then following with ethyl borate.

Identification and Properties of the Reaction Products

Pinocarvone: When prepared as described from the bisulfite it had the constants, b. p. 75-78° (3 mm.), 221-223° (760 mm.), d^{30}_4 0.980, α^{30}_D - 16.5°, n^{30}_D 1.5000, n^{20}_D 1.5038, M_D calcd. 44.83,[18] found 44.86.

Pinocarvoxime: This compound was prepared by the method of Beckmann.[34] One gram of hydroxylamine hydrochloride was dissolved in five ml. water, sodium bicarbonate was then added until evolution of carbon dioxide ceased. This solution was then shaken with one gram of carvopinone in three ml. methanol. After standing for two days the oxime was removed by filtration. On recrystallization from dilute ethanol, fine needles were obtained which melted at 68.0-68.4° (corr.). Schmidt[35] reported 68-69°.

Pinocarvone Semicarbazone: A saturated aqueous solution of semicarbazide hydrochloride and sodium acetate was prepared.[35] Ten ml. of this solution was added slowly to a solution of pinocarvone in methanol made by dissolving one gram pinocarvone on ten ml. methanol. Precipitation of the semicarbazone occurred immediately. The precipitate was collected and recrystallized from aqueous methanol, giving white needles, m. p. 212-213° (corr.), Schmidt[35] reported 212-215° C. The ketone was generated by steam distillation from a solution containing phthalic anhydride,[35] and was then distilled. None of its physical constants was changed appreciably.

Pinocarvone 2,4-Dinitrophenylhydrazone: Two grams of 2,4-dinitrophenylhydrazine was added to 100 cc. of an alcoholic solution containing 1.5 g. of pinocarvone. The mixture was brought to boiling and 2 cc. of concentrated hydrochloric acid added. This caused the formation of a semi-solid mass which was broken by violent agitation. After boiling for three minutes, the mixture was filtered and the precipitate washed with ethanol. The yield of crude material was about 70%, m. p. 221°. After two recrystallizations from boiling ethanol the m. p. reached the constant value of 223-223.5° (corr.). Anal. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.18; H, 5.50. Found: C, 58.10; H, 5.66.

Carvopinone: When this compound was prepared as described from the bisulfite solution it had the constants, b. p. 82-84°

(3 mm.), d^{30}_4 0.973, a ^{30}D + 62.7°, $n^{30}D$ 1.4910, $n^{21}D$ 1.4948, MD calcd. 44.83,[18] found 44.70.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.68, H. 9.45.

Carvopinone turned yellow upon standing for a few days and formed a white solid polymer when heated to 140° or on prolonged standing. This polymer is insoluble in the common solvents. Upon heating to about 320° it softens and slowly melts with decomposition.

Carvopinoxime: This compound was prepared by the method of Beckmann[34] as used for the preparation of pinocarvoxime. After recrystallization from aqueous methanol its m. p. was 132-133° (corr.). Wallach[36] reported 132°.

Carvopinone Semicarbazone: This compound was prepared by the method of Schmidt[35] described for the preparation of pinocarvone semicarbazone. It generally required two days for the semicarbazone to form. After recrystallization from aqueous methanol, the hard white prisms obtained did not melt below 300° as recorded by Wallach and Engelbrecht.[37]

Two grams of the substance was simultaneously hydrolyzed and steam distilled in the presence of oxalic acid.[35] A small amount of polymer formed in the flask - a behavior characteristic of carvopinone. The distillate was extracted with ether and the ether evaporated at room temperature under reduced pressure.

The oil obtained had the characteristic odor of carvone and a value $n^{20}D$ 1.4993. This oil was converted to the semicarbazone. The first crystals which formed were recrystallized from dilute methanol. These melted at 212-213°, indicating that some pinocarvone was present at this point. The remaining crystals softened at 154°, which is the approximate m. p. of the semicarbazone of dl-carvone,[38] and did not completely melt until 172° was reached. These facts indicate the formation of carvopinone, pinocarvone and carvone when carvopinone semicarbazone is hydrolyzed under the above conditions.

Separate experiments have shown that carvopinone does not yield carvone when refluxed with oxalic acid, or acetic acid, either in aqueous or alcoholic media. The product generally obtained by the above treatment was the characteristic polymer of carvopinone and some unreacted carvopinone.

For Pinocarveol: This compound obtained through the borate had the constants, b. p. 78-80° (3-4 mm.), $n^{25}D$ 1.4980, $(a)^{25}D$ + 65.5, d^{25}_4 0.976, M_D calcd.,[18] 45.52, found 45.72. This pinocarveol solidified at about 5° C. Schmidt reports a thaw point of 7° C. for pinocarveol purified through the phenylurethane.[35]

Pinocarveol phenylurethane was prepared as described by Schmidt.[35] Equivalents of the pinocarveol and phenyl isocyanate were mixed and allowed to stand for a day or two. The crystals of the urethane were then removed by suction, and recrystallized

from petroleum ether, b. p. 35-65° C. If the pinocarveol is not carefully purified, the urethane will crystallize with great difficulty, if at all. The m. p. of the impure urethane was 82-84°. Upon recrystallization from petroleum ether the m. p. is raised to 88-89° C. Palkin and Joshel[39] report 84-86° C. Schmidt[35] reports 84-85° and 88-90° for recrystallized products. For Pinocarvyl Acetate: This compound, when separated by the above described procedure, had the constants, b. p. 88-90° C. (2-3 mm.), 225° (corr.) (760 mm.), $n^{25}D$ 1.4750, d^{25}_4 0.991, $(a)^{25}_D$ -38°. Saponification number, calculated 194.26, found 195 (or 100.3%). Previously this compound has been characterized only by Schmidt[35] who reported, b. p. 227-8° C., d^{20} 0.997, (a) D + 15.8° for the d-isomer.

When prepared by the esterification of pinocarveol with acetic anhydride in the presence of sodium acetate[35] the constants are, b. p. 88-90° (2-3 mm.), $n^{25}D$ 1.4760, d^{25}_4 0.993, $(a)^{25}_D$ -20°. Saponification number, calculated 194.26, found 194 (or 100%).

Pinocarveol, like most secondary and tertiary terpene alcohols, will not readily esterify with acetic anhydride unless sodium acetate is present. This was verified by experiment. It will not esterify appreciably with glacial acetic acid in the presence of sodium acetate after refluxing for two hours.

Direct Preparation of Pinocarveol from β-Pinene

Pinocarveol was prepared by a modification of the procedure of

Palkin and Joshel.[39] Forty-seven grams of selenious acid was made by adding 6.6 grams water to 40.4 grams selenium dioxide. This was then added dropwise to a mixture of 120 g. B-pinene in 94 ml. absolute ethanol. During the addition the solution became warm and turned yellow. When the addition was complete, the mixture was refluxed for four hours. At the end of this time, the clear but reddish solution was steam distilled and the oil in the distillate was taken up in ether, washed, dried and distilled at 2-3 mm. pressure. This produced 37 g. (31% of the B-pinene) having the constants, n^{30}_D 1.4940, $(a)^{30}_D$ = + 57°. The material was then heated with 56 cc. of ethyl borate at 125° for one hour. The non-alcoholic portion was removed by simultaneously lowering the pressure and increasing the temperature to 150° C. The residue in the flask which was impure pinocarvyl borate, was hydrolyzed and simultaneously steam distilled from dilute sodium carbonate solution. The distillate was taken up in ether and distilled at 2-3 mm. pressure. This gave 21 g. of pinocarveol, which was 17.5% of original B-pinene or 75% of the impure material. The constants were, n^{25}_D = 1.4979, c^{25}_4 = 9.76, $(a)^{25}_D$ + 65.5, M_D calculated[18] 45.52, found 45.72. This pinocarveol was identical with that previously described.

The non-alcoholic portion of the oxidation mixture was distilled at 2-3 mm. pressure, giving 3.5 g. of an oil with n^{27}_D

1.4885, a_D ↓ 66°. This was impure carvopinone. It was then converted to the semicarbazone, which did not melt below 300°. The semicarbazone was then simultaneously hydrolyzed and steam distilled from oxalic acid. The distillate contained carvone, definitely proving that the non-alcoholic portion was largely carvopinone.

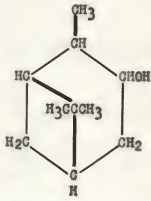
The Action of Selenium Dioxide on Pinocarveol

Twenty-five grams of pinocarveol were dissolved in 75 cc. ethanol in a flask equipped with a reflux condenser and mechanical stirrer. Ten grams of selenium dioxide were slowly added. Upon heating, the solution first turned yellow, then red and finally brown. After refluxing for five hours, three and one-half grams of selenium were obtained and the liquid portion was steam distilled. This gave 15 g. of an oil b. p. 84-85° (3-4 mm.), n^{25}_D 1.4931, d^{25}_4 0.982, a_D ↓ 60.5° (10 cm. tube). This was largely impure carvopinone which was purified through the bisulfite compound to give 6.1 g. of carvopinone, b. p. 84-85° C. (3-4 mm.), n^{25}_D 1.4935, d^{25}_4 0.981, $(a)^{25}_D$ ↓ 62.7°. About 0.3 g. pinocarvone was isolated, this had n^{25}_D 1.5010. Approximately one-half gram of oil was not extracted by the bisulfite. Judging by its refractive index, n^{25}_D 1.4940, and its action to heat, it was impure carvopinone.

Reduction Experiments

d-cis Pinocampheol is formed in nearly theoretical yield by

the catalytic hydrogenation of pinocarveol in cyclohexane using a 10% palladium on charcoal catalyst[40] and heating the mixture



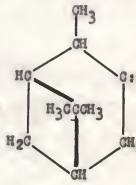
d-cis Pinocampheol

at 100° C. under a hydrogen pressure of 1200 pounds per square inch for two hours in a bomb. The catalyst was removed by filtration and the pinocampheol purified by distillation at reduced pressure. The constants were, m. p. 55.5-56.0° C., $n^{25}D$ 1.4830 (super cooled) (a)^{25}D + 39° (10.5% in ether). The a-naphthyl urethane was prepared by allowing equimolecular amounts of a-naphthylisocyanate and pinocampheol to stand until solid. This solid was filtered and recrystallized from petroleum ether, boiling range 35-65° C. The a-naphthylurethane had a m. p. of 85.5-88.0° C. (corr.) which is the same as that reported by Kuwata[41] and Schmidt and Schultz[42] for d-cis pinocampheol.

d-cis Pinocamphyl acetate may be prepared quite pure by the catalytic reduction of pinocarvyl acetate under the conditions described above. The reduction product is purified from the solvent by distillation at reduced pressure. It had the constants,

b. p. 80-82° C. (2-3 mm.), 227-8° C. (corr.) (760 mm.), n^{21}_D 1.4641, d^{25}_4 0.979, $(\alpha)^{25}_D$ 23°. Saponification number, calculated 196.28, found 197 (or 100.3%). Upon saponification, this ester produced d-cis pinocampheol whose constants were in close agreement with those above. Kuwata[41] reports for l-cis pinocamphyl acetate, b. p. 82-84° (3 mm.), d^{20}_4 0.9781, n^{20}_D 1.4638.

l-trans Pinocamphone is obtained by the catalytic hydrogenation of carvopinone by the procedure described above.



l-trans pinocamphone

The product was purified by washing with neutral bisulfite and distilling the unextracted oil at 2-3 mm.; b. p. 212° C. (corr.) (760 mm.), n^{25}_D 1.4735, d^{25}_4 0.964, $(\alpha)^{25}_D$ -13.5°. Its semicarbazone recrystallized as very fine white needles from dilute methanol, m. p. 227.5-228.0° (corr.). Schmidt and Schultz[42] report for the semicarbazone of l-trans pinocamphone the m. p. 227° C. and for the semicarbazone of l-cis pinocamphone, 219° C. Hence, carvopinone on reduction gives rise to the trans isomer.

Another pinocamphone was obtained upon the reduction of pino-

carvone under the same conditions. It had the constants b. p. 75° (2-3 mm.), n^{29}_D 1.4772, a_D -29° (10 cm. tube). It forms a semicarbazone melting at 185°. This is apparently the B- form of the semicarbazone described by Gildemeister and Kohler.[43] The a- form described by these authors has a m. p. of 218-219° which corresponds to the semicarbazone of cis pinocamphone of Schmidt and Schultz. Thus this pinocamphone is the B-form of cis pinocamphone.

Discussion

In this chapter new methods for the preparation of pinocarvone, carvopinone, pinocarveol, pinocarvyl acetate and their reduction products have been described. Previously the preparation of pinocarvone involved the oxidation of pinocarveol by dichromate, a process which did not give good yields. Pinocarveol was generally obtained from natural sources or by the catalytic air oxidation of B-pinene. Pinocarvyl acetate had previously been prepared only by direct esterification of pinocarveol. Carvopinone, which up to the present work had not been characterized, was a chemical curiosity due to its difficulty of preparation as already mentioned.

When the B-pinene and selenium dioxide are used in equimolecular amounts in the presence of a non-esterifying solvent the only steam volatile products of the reaction are carvopinone

and pinocarvone. Table XIII lists data for experiments in various non-esterifying media using equimolecular proportions of reactants.

In column 7 of Table XIII are listed the percentages of carvopinone in the oxidation product as based on Biot's rule for mixtures.

$$x = \frac{(a)_0 - (a)_2}{(a)_1 - (a)_2}$$

where

x = mole fraction carvopinone

$(a)_0$ = specific rotation of the mixture

$(a)_1$ = specific rotation of pure carvopinone

$(a)_2$ = specific rotation of pure pinocarvone

These calculations were verified by the estimation of the quantity of carvopinone obtained in each reaction. Thus one needs only to determine the specific rotation of the steam volatile oil in order to ascertain the proportions of the two ketones.

With but one exception, the longer the reaction continues the larger is the percentage of pinocarvone in the steam volatile oil. This is probably due to the fact that carvopinone is unstable and polymerizes rather readily.

The yield of steam volatile oil vs. time indicates a maximum depending on the temperature of the reaction. This is verified by the fact that when the reaction was carried out for 48 hours

in ethanol the yield of oil was only about 5%. In general, the most satisfactory time of reaction is about ten hours.

No definite conclusions can be drawn concerning the effect of the volume of solvent used, but it is believed that this effect is negligible in these experiments.

Of definite interest is the observation that a successful oxidation takes place in pyridine. This is in contrast to the findings of Guillemonat[26] for ethylenic hydrocarbons.

The properties of the oxidation mixtures obtained in ethanolic medium agree with those reported by Dupont, Allard and Dulou,[49] and it appears probable that their oil was a mixture of the ketones. Furthermore, the refractive index, density and molar refraction reported by them are between those of the pure compounds. The semicarbazone of carvopinone forms much more slowly than that of pinocarvone so that the first crystals obtained from the oil will give a melting point corresponding to the semicarbazone of pinocarvone. It was probably in this manner that they reported the correct value for the melting point of the semicarbazone of pinocarvone.

When B-pinene and selenium dioxide are allowed to react in such a proportion that one-half mole selenium dioxide is present for each mole of B-pinene, the product is largely pinocarveol with a small amount of carvopinone.

A study of Table XIV will show that the effect of the selenium

dioxide B-pinene ratio in esterifying solvents was not nearly as pronounced as it was for ethanol.

It may also be seen from Table XIV that the major portion of the steam volatile oil is pinocarvyl acetate when the reaction is carried out in acetic media. This finding is in accord with the mechanism proposed by Guillemonat[26] for the oxidation of ethylenic hydrocarbons in which a selenium complex is formed with the hydrocarbon. This, in turn, is decomposed by the solvent. In this case it results in the formation of pinocarvyl acetate.

Water is a product of the reaction in which the selenium complex is formed. A reaction between the complex and the water thus formed would account for the formation of pinocarveol. As already pointed out pinocarveol is not esterified by acetic acid and the alcohol therefore becomes subject to oxidation by selenium dioxide. This would account for the formation of the two ketones.

It is believed that this latter oxidation also takes place through the medium of a selenium complex. This is supported by the fact that the reaction mixture becomes yellow, then red and finally deposits selenium, and upon steam distillation leaves a non-volatile selenium compound.

Since carvopinone yields trans pinocamphone upon reduction, it may be seen by setting up a model that the carvonyl group of carvopinone is close to the gem-dimethyl group. This proximity would tend to hinder the rate of reaction of the carbonyl group with

large molecules. The slowness of the reactivity of the carbonyl group was pointed out previously in respect to the formation of the semicarbazone. This steric relation may also be the cause of the relative ease of the rupture of the cyclobutane ring to form carvone, and cause its ready polymerization.

The pinocarveol formed by the action of selenium dioxide on β-pinene is probably the trans form with respect to the hydroxyl group and the gem-dimethyl group. It is believed that the method of formation would tend to give rise to the more stable form, which is trans, and to the assumption that if the pinocarveol were cis, the reduction product would be cis with respect to hydroxyl and gem-dimethyl groups and cis with respect to methyl and gem-dimethyl groups. Such an arrangement would be expected to be unstable.

TABLE XIII

All oxidations listed were between 0.5 mole of β-pinene and 0.5 mole of selenium dioxide except the reaction described in the second line which was between 1 mole of β-pinene and 1 mole of selenium dioxide.

Solvent	Solvent in cc.	Reaction in hr.	% Se recov.	Yield, %	Steam volatile oil $(\alpha)^{30}_D$	Steam volatile oil Biot % carvopinone[a]
Ethanol	200	3	45	19	43	75
Ethanol	300	10	60	30	16	41
Acetone	100	10	29	23	49	83
Benzene	100	10	55	15	46	79
Hexane	100	10	50	18	54	89
Ether[b]	100	10	13	17	59	95
Ether[b]	100	48	40	28	56	91
Ether[b]	200	72	64	25	55	90
Ether[b]	100	168	55	24	57	93
Carbon tetr.	100	10	10	28	56	91
Pyridine	100	10	95	34	56	91
Water	100	10	0.0	24	56	91
None	...	10	0.0	27	50	84

[a]Carvopinone $(\alpha)^{30}_D$ + 62.7°; pinocarvone $(\alpha)^{30}_D$ -16.5°.
[b]Solvent loss was about 0.5 cc. per hour.

TABLE XIV

OXIDATIONS IN ESTERIFYING MEDIA

All oxidations listed were between 1 mole B-pinene and one-half mole selenium dioxide except the first reaction which was between one mole B-pinene and one mole selenium dioxide and the second reaction which was between 0.5 mole B-pinene and 0.5 mole selenium dioxide.

Solvent	Grams Se Recovered	Steam Volatile oil g.	% Steam Pino-carveol	Volatile Oil Recovered As Pinocarvyl acetate	Carvo-pinone	Pino-carvone
Ac_2O	49	68	0.6	65	1	3.7
HAc	20	14.5		20		
Ac_2O	5	53	None	66	1	2
HAc	None	41	3.7	22	20	2
HAc + Ac_2O	6	27	13	44	2	8.5

Summary

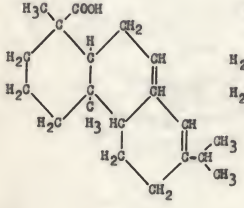
The procedures developed for the oxidation of B-pinene by selenium dioxide have been described. A new method for the preparation of carvopinone was developed. A method for the separation of carvopinone from pinocarvone was discovered and developed. Carvopinone, pinocarvone, pinocarveol, pinocarvyl acetate, and pinocamphyl acetate have been more completely characterized than heretofore. By means of catalytic reduction the geometric configuration of the oxidation products were ascertained. A proposal as to the means of formation of the oxidation mixtures has been presented.

Chapter IV

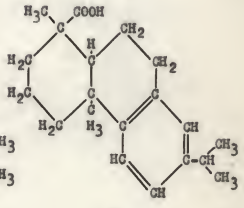
PREPARATION OF AZO DYES FROM ROSIN

This chapter describes a method for the preparation of azo dyes from rosin. The principle steps involve the successive preparation of abietic acid, pyroabietic acid, 6-sulfodehydroabietic acid, 6-sulfo, 8-nitrodehydroabietic acid, and 6-sulfo, 8-aminodehydroabietic acid. This last acid may be diazotized and coupled with aromatic substances which have an active ortho or para hydrogen to form azo dyes. This problem was first mentioned in 1939[55].

The starting material, rosin, is largely abietic acid (I). By disproportionation of the abietic acid, dehydroabietic acid (II) is obtained. This latter acid, due to its aromatic ring, may be nitrated and sulfonated to yield a nitro sulfonic acid. This nitro acid could then be reduced, diazotized and coupled to give rise to dyestuffs.



(I)



(II)

When abietic acid is submitted to heat treatment for about 300 hours at 250° C. it becomes stabilized; that is, it is not subject to discolorization by continued standing or exposure to the air as is abietic acid[45]. This stabilized acid is sometimes called alpha pyroabietic acid[45, 46]. Fleck and Palkin[47] have recently shown that the same alpha pyroabietic acid is produced by the action of palladium on charcoal on abietic acid in about forty minutes at temperatures around 250° C. When the temperature is carefully controlled and is not allowed to exceed 225° C., the disproportionation is complete and may be qualitatively expressed by the equation:

$$\underset{\text{Abietic}}{C_{20}H_{30}O_2} \longrightarrow \underset{\text{Dihydro-abietic}}{C_{20}H_{32}O_2} + \underset{\text{Dehydro-abietic}}{C_{20}H_{28}O_2} + \underset{\text{Tetrahydro-abietic}}{C_{20}H_{34}O_2}$$

If the temperature is allowed to rise to about 250° C. the amount of dehydroabietic acid in the pyroabietic acid is increased at the expense of the formation of the other acids. This increase can be continued until a temperature of 275° C. is reached. Much hydrogen is evolved as the catalyst rapidly assumes the role of a dehydrogenation promoter at this temperature. If the temperature should exceed 275° C. decarboxylation and demethylation will occur.

Dehydroabietic acid is obtained from the pyroabietic acid by a sulfonation process first investigated by Hasselstrom[48] and developed in more detail by Feiser and Campbell[28, 49]. In this process, the entire mixture is treated with concentrated sulfuric

acid at -10 to -5° C. for about forty minutes. The aromatic ring of dehydroabietic acid is sulfonated at the six position. The sulfonic acid is then removed and crystallized. Upon strong acid hydrolysis of the sulfonic acid, dehydroabietic is formed.

Instead of using dehydroabietic acid as the starting material for a dyestuff preparation, as did Litmann[53], it was decided that the sulfonic acid from which dehydroabietic acid is prepared would be a more satisfactory starting material. This was due to the larger yield of final product when based on the starting amount of abietic acid. Another advantage obtained by using the sulfonic acid is that the solubilizing group is already present in the molecule and will not need to be added after the production of the dyestuff.

6-Sulfodehydroabietic acid was therefore nitrated and reduced to 6-sulfo, 8-aminodehydroabietic acid. This was diazotized and coupled with dimethylaniline, a-naphthol, B-naphthol, and 2-naphthol-6-sulfonic acid.

It might be mentioned that this amino sulfonic acid could be converted into sulfonamides, however a para substituted compound would be more satisfactory. A para compound could be prepared by the following procedure: form the dinitro derivative of dehydroabietic acid, reduce with ammonium sulfide to form 6-amino, 8-nitrodehydroabietic acid, diazotize and remove nitrogen to give 8-nitrodehydroabietic acid. Reduce the mononitro compound to the amine, sulfonate and obtain 5-sulfo, 8-aminodehydroabietic acid. Another method that might be satisfactory would be to sulfonate the diamino

compound and then remove one of the amine groups by diazotization.

Preparation of Abietic Acid

This was prepared by a modified Steele's method[50, 51]. Five pounds of technical abietic acid were refluxed with 1500 ml. of glacial acetic acid for two hours and then allowed to crystallize. The crystals were collected and washed with ice cold 9 to 1 ethanol and then recrystallized from acetone. The crystals from acetone were dissolved in 2500 ml. of ethanol and sufficient sodium hydroxide added to the hot solution to form the quarter sodium salt of abietic acid. When cool, the crystallized quarter salt was dried and then heated with enough water to cover the crystals, filtered and dried. The quarter salt was then placed in 1000 ml. of acetone and an excess of concentrated hydrochloric acid was added. Upon heating the solid disappears and two layers are formed, the upper layer containing an acetone solution of abietic acid is removed and the abietic acid is allowed to crystallize out. This was dried and stored in vacuum. Its constants were, m. p. 160-164° C., $(\alpha)^{25}_{D}$ -91° (0.447 g. in 20 grams ethanol).

Preparation of Pyroabietic Acid

A palladium and charcoal catalyst prepared by dissolving 5 grams of palladious chloride in 100 ml. water and adding 27 grams of Norit. After boiling for two hours it was cooled and then reduced with hydrogen at atmospheric pressure[40].

One hundred and fifty six grams of abietic acid was mixed with 3.2 grams of the above catalyst and heated at 260-270° C. for one hour. The mixture was allowed to cool, dissolved in ethanol and filtered to remove catalyst. The filtrate was heated to the boiling point and water was added to incipient turbidity. Upon cooling 148 grams of pyroabietic acid were collected. Its constants were, m. p. 171-172° C., $(\alpha)^{25}_{D}$ + 50° (0.625 g. in 20 grams ethanol). These constants are in agreement with those of Fleck and Palkin[45, 46] and Feiser and Campbell[28].

Preparation of 6-Sulfodehydroabietic Acid

One hundred and sixty grams of pyroabietic acid were then powdered and added to 1440 grams of ice cold concentrated sulfuric acid[48]. This mixture was mechanically stirred and held at a temperature of 5° C. for forty minutes. At the end of this time the mixture was poured into twice its volume of crushed ice and filtered. The precipitate was washed with cold water until the filtrate became turbid. The precipitate was then air dried for one day and then dissolved in boiling acetic acid. The hot acetic acid solution was filtered through cotton to remove oils and other neutral materials. Upon cooling, fine needle shaped crystals of the sulfo-acid were formed. The crystals were collected, washed with ether to give a very white product. This sulfonic acid is largely a mono-hydrate, as the sulfur analysis shows 8.07% sulfur where the mono-

hydrate should theoretically contain 8.04% sulfur. Feiser and Campbell[49] and Hasselstrom[48] have shown that the sulfo-acid crystallizes from water as the trihydrate. A yield of 133 grams of the monohydrate was obtained having a melting point of approximately 248° C. The melting point is not sharp and is accompanied by decomposition as is characteristic of sulfonic acids.

In order to definitely establish this acid as 6-sulfodehydroabietic acid it was converted to the dimethyl ester. A small amount of the acid was suspended in ether in a flask into which an etherial solution of diazomethane was distilled. When the suspended material disappeared, the flask was removed and the ether evaporated. The crystals of the dimethyl ester were then recrystallized from methanol giving a product, m. p. 177.0-177.5° C. Feiser and Campbell[28] have reported the m. p. 175-176°C. for this compound.

Preparation of 6-Sulfo, 8-nitrodehydroabietic Acid

The purified sulfonic acid was added to cold concentrated sulfuric acid in the proportions, 4.35 grams of sulfo-acid to 27 grams of sulfuric acid[52]. When addition was completed and a homogenous solution obtained, concentrated nitric acid was added to the solution. Exactly enough nitric acid was used to form the mononitro derivative of the sulfo-acid started with. After fifteen

minutes the nitration mixture was poured onto four times its volume of crushed ice and filtered. The precipitate was washed thoroughly with 3 to 1 hydrochloric acid. It was then dissolved in boiling water and filtered to remove any dinitro compound that was formed by the nitration. The filtrate which contained a solution of 6-sulfo, 8-nitrodehydroabietic acid was evaporated nearly to dryness. The product was gelatinous and was difficultly dried. It may be dried over phosphorus pentoxide in vacuo. Since a dry product was not essential, this process was carried out with only a small portion.

Experiment showed that this nitro acid cannot be hydrolyzed to 8-nitrodehydroabietic acid by the procedure of Feiser and Campbell[28] for preparing dehydroabietic acid.

Preparation of 6-Sulfo, 8-aminodehydroabietic Acid

The moist 6-sulfo, 8-nitrodehydroabietic acid was reduced to 6-sulfo, 8-aminodehydroabietic acid. The reduction was carried out both chemically and catalytically.

The chemical reduction was made by suspending the nitro compound in concentrated hydrochloric acid and adding an excess of granulated tin. The mixture was then heated on a steam bath for four hours, at the end of which time the mixture was made neutral with 25% sodium hydroxide solution. Enough concentrated hydrochloric acid was added to cause a thorough precipitation. The precipitate

was collected and washed with a little dilute hydrochloric acid and then air dried. This washing should remove some of the unreduced nitro acid as it is more soluble in water than is the amino acid. The 6-sulfo, 8-aminodehydroabietic acid obtained in this manner has a pale brownish color. It is insoluble in most organic solvents. It is alkali soluble and somewhat soluble in dioxane and ethanol. Analysis of a sample dried in vacuo over phosphorus pentoxide gave 4.7% sulfur, calculated for $C_{20}H_{29}O_5NS$ 7.9% (Parr bomb) and 2.6% nitrogen, calculated 3.5% (Kjeldahl).

These figures correspond to about 65% amino acid. The impurities are probably unnitrated sulfoacid and unreduced nitro acid, plus some decomposition products. This impure product is to be expected from the nature of the method of preparation.

A pure sulfo-amino acid should result if the sulfo-nitro acid were esterified with diazomethane, followed by catalytic reduction of the nitro group and then hydrolysis of the dimethyl ester.

The quantities used were 64 grams of crude sulfo-nitro acid in 100 grams of concentrated hydrochloric acid to which 38 grams of metallic tin were added. Since the product was gelatinous and was dried with difficulty, no yield was estimated.

The catalytic reduction required the preparation of reasonably dry sulfo-nitro acid. The dry compound was dissolved in dioxane, Raney nickel catalyst added and hydrogenated in the bomb. The amino

was obtained by diluting the dioxane solution of acid and catalyst with three times its volume of water and evaporating. After removal of the catalyst the amino acid was filtered off from time to time during the evaporation. The residue was discarded as the unreduced nitro compound was concentrated in this portion.

The quantities used for the catalytic preparation were: 33 grams of 6-sulfo, 8-nitrodehydroabietic acid in 300 ml. dioxane. Four grams of Raney nickel were used. The reaction was carried out at a hydrogen pressure of 1000 pounds per square inch at 125° C. for four hours.

Diazotization of 6-Sulfo, 8-aminodehydroabietic Acid

Ten grams of the amino acid were dissolved in 100 ml. of ten percent sodium hydroxide solution and then a ten percent solution of sodium nitrite were added until 0.7 moles of this reagent were present per mole of amino acid. Enough crushed ice was then added to keep the mixture at about 3-5° C. and then 35 ml. of concentrated hydrochloric acid were slowly added with constant stirring. After the mixture stood ten minutes it was tested for the presence of free nitrous acid with starch iodide paper. If the test was negative more sodium nitrite was added dropwise until a positive test was observed. This produced a suspension of a light yellow diazonium compound. Aliquots of this suspension were then used for the following coupling reactions.

Coupling of the Diazotized 6-Sulfo, 8-aminodehydroabietic Acid

With Amines:

A solution of the amine was made in ten percent hydrochloric acid so that each ml. of the solution was equivalent to 0.1 gram of the amine. The exact amount of this solution calculated for the aliquot of the diazo suspension used was cooled to 3-5° C. and the diazo suspension was slowly added. When the addition was complete, sodium carbonate solution was added until carbon dioxide no longer was rapidly evolved. The cold and almost neutral solution was then stirred for a half hour, made definitely alkaline, saturated with sodium chloride and filtered.

When coupled with dimethylaniline this procedure gave an orange yellow dye. Its dilute aqueous solution is pale green in acid and orange in alkali.

With Phenols:

A solution of the phenol was made so that each ml. of a ten percent sodium hydroxide solution would contain 0.1 gram of the phenol. The calculated volume of this solution required to couple with the aliquot of the diazo suspension was then cooled to 3-5° C. To the cold solution was then added with stirring the diazo suspension. After standing for thirty minutes the solution was saturated with sodium chloride, evaporated and filtered. The precipitate was air dried on a clay plate.

When coupled with α-naphthol this procedure gave a brown dye. Its dilute aqueous solution is red in acid and brown in alkali.

β-naphthol gave a brown dye which was red in acid and yellow brown in alkali.

2-Naphthol 6-sulfonic acid gave an orange dye which is deep red in alkaline solution and red orange in acid solution.

To prove that the colored compounds thus formed were azo compounds, the following two tests were performed[54].

A small spatula full of the azo dye was suspended in 1 ml. of water to which a small quantity of sodium hydrosulfite was added. The mixture was heated until no further change occurred. By extraction of the mixture a small amount of diamine or aminophenol was obtained, as indicated by solubility, odor and reaction to ferric chloride.

An azo compound will add sodium bisulfite whereas other substances reducable by the above procedure will not.

The addition was carried out by adding two drops of a ten percent sodium hydroxide solution to 1 ml. of saturated sodium bisulfite solution and then heating. A few drops of an aqueous solution of the azo compound were then added and again heated. This produced an addition product which was either colorless or faintly colored in comparison to the original azo compound.

Summary

The preparation of azo dyes by diazotizing 6-sulfo, 8-aminodehydroabietic acid, prepared from rosin, and coupling with amines and phenols has been described.

A detailed procedure for the method used to obtain 6-sulfo, 8-aminodehydroabietic acid has been given.

A new compound, 6-sulfo, 8-aminodehydroabietic acid has been reported and partially characterized.

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BIOGRAPHICAL ITEMS

William David Stallcup was born October 25, 1913 in Cleveland, Ohio. He attended the public schools of St. Petersburg, Florida. In 1934 he was graduated from the University of Florida with the degree of Bachelor of Science. He received the degree of Master of Science in August 1938. His work for the Master's degree was carried out in summer sessions from 1934 through 1938; during the regular sessions he taught chemistry at the St. Petersburg, Florida Senior High School.

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COMMITTEE REPORT

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Date May 25, 1942

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